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From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

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United States Patent and Trademark Office, PCT
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in its capacity as elected Office

Date of mailing (day/month/year) 12 March 2001 (12.03.01)	
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International filing date (day/month/year) 12 July 2000 (12.07.00)	**Priority date** (day/month/year) 13 July 1999 (13.07.99)
Applicant HODES, Gary et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

29 January 2001 (29.01.01)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 9932 PCT	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/IL 00/ 00408	International filing date *(day/month/year)* 12/07/2000	(Earliest) Priority Date *(day/month/year)* 13/07/1999
Applicant YEDA RESEARCH AND DEVELOPMENT CO. LTD. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.
   [ ] filed together with the international application in computer readable form.
   [ ] furnished subsequently to this Authority in written form.
   [ ] furnished subsequently to this Authority in computer readble form.
   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).
3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

   [X] the text is approved as submitted by the applicant.
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5. With regard to the **abstract**,

   [X] the text is approved as submitted by the applicant.
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6. The figure of the **drawings** to be published with the abstract is Figure No. ______

   [ ] as suggested by the applicant.
   [ ] because the applicant failed to suggest a figure.
   [ ] because this figure better characterizes the invention.

   [X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IL 00/00408

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C25B1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 33871 A (UNIVERSITE LIBRE DE BRUXELLES) 14 December 1995 (1995-12-14) page 17 -page 19; claims 1-14 ---	1
A	J. REISSE: "Quantitative sonochemistry" ULTRASONICS SONOCHEMISTRY, no. 3, 1996, pages 147-151, XP002153735 page 149, paragraph 4 -page 150 page 150; example 9; table 2 ---	1
A	DE 38 26 281 A (HAHN-MEITNER-INSTITUT BERLIN GMBH) 1 February 1990 (1990-02-01) column 3 -column 4; claims 1-11 -----	1,10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 November 2000	05/12/2000

Name and mailing address of the ISA	Authorized officer
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1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9533871	A	14-12-1995	BE	1008304 A	02-04-1996
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(71) Applicant *(for all designated States except US)*: **YEDA RESEARCH AND DEVELOPMENT CO. LTD.** [IL/IL]; Weizmann Institute of Science, P.O. Box 95, 76100 Rehovot (IL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **HODES, Gary** [IL/IL]; 76830 Ganei Hadar (IL). **MASTAI, Yitzhak** [IL/IL]; Louie Marchal Street 35, 62000 Tel-aviv (IL). **HOMYONFER, Moshe** [IL/US]; 768 Madison Avenue, New York, NY 10021 (US). **TENNE, Reshef** [IL/IL]; Hashomrim Street 21, 76231 Rehovot (IL).

(74) Agent: **BEN-AMI, Paulina**; Yeda Research and Development Co. Ltd., Weizmann Institute of Science, P.O. Box 95, 76100 Rehovot (IL).

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(54) Title: SONOELECTROCHEMICAL SYNTHESIS OF INORGANIC FULLERENE-LIKE NANOPARTICLES OF METAL CHALCOGENIDES

(57) Abstract: Inorganic fullerene-like (IF) nanoparticles of metal chalcogenides, particularly molybdenum sulphide, including one or more layers of desired sizes and shapes, e.g., spheres, sphere-like, nanotubes and polyhedral shapes, are manufactured by sonoelectrochemical liquid-phase synthesis comprising: (a) dissolving in a suitable solvent: (i) at least one compound of said metal and at least one compound of said chalcogen, or (ii) at least one said chalcogen-containing said metal compound; (b) immersing an electrically conductive ultrasonic probe in the solution obtained in (a); (c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of said electric power supply is connected to a counter electrode; (d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode; and (e) recovering the IF-metal chalcogenide structures that precipitated in step (d).

SONOELECTROCHEMICAL SYNTHESIS OF INORGANIC FULLERENE-LIKE NANOPARTICLES OF METAL CHALCOGENIDES

FIELD AND BACKGROUND OF THE INVENTION

The present invention relates in general to a method for preparing inorganic fullerene-like structures of metal, e.g. transition metal, chalcogenides, particularly, to sonoelectrochemical synthesis of such inorganic fullerene-like structures, and more particularly to room temperature sonoelectrochemical synthesis of molybdenum sulphide.

Since the discovery of the original fullerenes, C_{60} and C_{70} [1] and, retrospectively, multi-shell closed carbon structures [2], a wide range of related fullerene-like structures have been identified. These include closed structures of other materials such as WS_2 [3], MoS_2 [4], $NiCl_2$ [5] and other shapes, in particular nanotubes, of many of the above materials [1,3,5,6] as well as of BN [7] and VO_x.[8] All these closed structures require high temperatures for their formation to provide the high energy needed for their closure. Methods used to provide these temperatures include, besides the arc discharge technique commonly used for carbon fullerenes [9], laser vaporization [1] and heating in a furnace.[3,4] Other techniques, based on local heating, include electron [10] and ion beam [11] treatment and high electric current densities from an STM tip.[12] Room temperature crystallization of amorphous WS_3 into closed structures of WS_2 has been reported to occur over several years [10], demonstrating the thermodynamic stability of these structures, but illustrating the large kinetic barriers for their formation.

Particles of inorganic structures having a layered configuration (a single layer or nested layers) are known as inorganic fullerenes (IF). For ease of discussion, inorganic layered structures such as, but not limited to, spheres, whiskers, nanotubes, polyhedral and others, will interchangeably be referred to as "inorganic fullerene-like" or "IF" materials, throughout the specification.

Nanoclusters of IF metal chalcogenide materials, such as WS_2 and MoS_2, were recently described (Refs. 3 and 10 herein and EP 0 580 019). Thus, according to European Patent No. 0 580 019 of the same applicants, a method was described for the preparation of oriented thin films of the transition metal chalcogenides WS_2, WSe_2, MoS_2 and $MoSe_2$ from the corresponding metal oxides, whereby in some conditions the nanoclusters of the layered IF metal chalcogenide materials were shown to be unstable against folding and to close upon themselves to form nested IF nanoparticles such as nested fullerene-like structures and nanotubes. These conditions could not be controlled and thus the method according to the above-mentioned publications do not allow to obtain high yields of macroscopic quantities of the IF metal chalcogenide, nor to determine the size and shape of the particles.

A gas phase synthesis for the preparation of a few milligrams of IF-MoS_2 from a molybdenum trioxide precursor and H_2S in a reducing atmosphere has been described, [4] taking advantage of the sublimation of the molybdenum suboxide (MoO_{3-x}) under reducing conditions above 700 ^oC. Thus, a portion of 30 mg of MoO_3 powder (>99% pure) was heated (>800 ^oC) and slowly reduced to MoO_{3-x} by a stream of forming gas (typically 5%H_2/95%N_2. The suboxide (MoO_{3-x}) sublimed and effused out of a nozzle where it crossed a stream of H_2S gas mixed with a forming gas. After some 3-5 minutes, the entire load (30 mg) of MoO_3 sublimed, the reaction products were collected on a quartz substrate, positioned few cm away from the crossing point of the two gas streams and maintained at the same temperature (>800 ^oC), and the collected nanoparticles were progressively converted into nested layer polyhedra within ca. 30 minutes of firing time. The average size of the oxide particles and the ensuing IF-MoS_2 particles increased with temperature. It was found that above 900 ^oC, platelets with 2H-MoS_2 structure abound, and became the sole product above 950 ^oC. According to the above-described gas phase reaction it is difficult to obtain very high quantities of

the IF structures of transition metal chalcogenides. The IF particles have several interesting and useful applications, and it would be very advantageous to have a method and apparatus for high yield preparation of macroscopic quantities of IF particles of metal, e.g. transition metal, chalcogenides.

The use of ultrasonic radiation to increase the rate of chemical reactions is well known and related to the phenomenon of cavitation, whereby very high local temperatures and pressures are transiently formed (sub-μs) in collapsing bubbles.[13] More recently, the combination of sonochemistry and electrochemistry (sonoelectrochemistry) has been investigated. Among the characteristics of this technique are acceleration of mass transport, cleaning and degassing of the electrode surface and increased reaction rates.[14] Sonoelectrochemical formation of nanoscale metal powders [15] has been accomplished by applying an electric current pulse to nucleate the electrodeposit, followed by a burst of ultrasonic energy which removes the metal particles from the sonic probe cathode.

SUMMARY OF THE INVENTION

Based on the assumption that the short bursts of local high temperature may allow formation of closed structures at nominal room temperature, we used the known process for cathodic electrodeposition of MoS_2 from solutions of thiomolybdate ions.[16,17] The MoS_2 deposited using this technique is normally amorphous as deposited and becomes crystalline after heat treatment forming a highly-textured film.[17] This high degree of texture suggests a planar structure.

Using the same basic technique, but depositing onto an ultrasonic probe using the principle described above of a current pulse followed by an ultrasonic pulse to remove the deposit from the probe/electrode, it was found that a black deposit of molybdenum sulphide formed in the solution.

It should be noted that the term "inorganic fullerene-like" ("IF"), as used herein in the specification and claims, refers to inorganic metal chalcogenide structures having one layer or nested layers which form what is known in the art as a closed cage [3] which may encage a void (i.e., be hollowed) or a core or may form

a stuffed nested layer structure, i.e. a structure containing a material other than the metal material precursor encaged within nested layers of the metal chalcogenide. In particular the term refers to structures such as what is known in the art as single and double layer inorganic fullerenes, nested layers inorganic fullerenes, stuffed inorganic fullerenes, single layer nanotubes, nested nanotubes, stuffed nanotubes, and inorganic supperlattice structures, i.e. IF particles having layers of two or more different chalcogenides of the metal, e.g. WS_2 and WSe_2.

According to the method of the present invention, IF nanoparticles of metal chalcogenides including one or more layers of desired sizes and shapes, e.g., spheres, sphere-like, nanotubes and polyhedral shapes, may be manufactured.

The metals that are suitable for this method are metals that form layered metal chalcogenide products such as In, Ga, Sn and a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru.

The present invention thus relates to a method for the sonoelectrochemical liquid phase synthesis of inorganic fullerene-like (hereinafter IF) structures of metal chalcogenides, wherein said metal is selected from In, Ga, Sn and a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru, and the chalcogen is S, Se or Te, the method comprising the steps of:

(a) dissolving in a suitable solvent: (i) at least one compound of said metal and at least one compound of said chalcogen, or (ii) at least one said chalcogen-containing said metal compound;

(b) immersing an electrically conductive ultrasonic probe in the solution obtained in (a);

(c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of said electric power supply is connected to a counter electrode;

(d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode: and

(e) recovering the IF metal chalcogenide structures that precipitated in step (d).

The solvent in step (a) may be aqueous or non-aqueous. Examples of non-aqueous solvents are, but not limited to, alcohols and dimethyl sulfoxide (DMSO). The synthesis is carried out at a temperature in which said solvent is in the liquid state. For example, when the solvent is water, the synthesis may be carried out at room temperature.

The ultrasonic probe is preferably a Ti probe. In a preferred embodiment, in step (d), first an electric voltage is applied to both the ultrasonic probe electrode and the counter electrode and is then followed by an ultrasonic signal to the ultrasonic probe electrode, and the sequences of electric voltage and ultrasonic signal are repeated until the desired amount of IF-metal chalcogenide structures is obtained.

In another preferred embodiment, the ultrasonic probe electrode is connected to the negative terminal of the electric power supply and the counter electrode is connected to the positive terminal.

As described above, the metals that are suitable for this method are metals that form layered metal chalcogenide products. Examples of metal chalcogenides that form layered products and are suitable for the preparation of IF structures according to the method of the invention include, but are not limited to, WS_2, WSe_2, MoS_2, $MoSe_2$, SnS_2, $SnSe_2$, RuS_2, GaS, GaSe, In_2S_3 , In_2Se_3 , InS, InSe, etc. [for additional examples, see A. F. Wells, Structural Inorganic Chemistry, 5th edition, Oxford Science Publications (1993); Chemistry of the Elements, by N. N. Greenwood and A. Earnshaw, Pergamon Pres, Oxford (1990)].

The metal compound according to the invention may be an oxide that is soluble in an electrolyte, for example MoO_3 and WO_3, that are soluble in alkaline solutions.

The chalcogen according to the invention is S, Se or Te, and the chalcogen compound may be a chalcogen, a compound containing a chalcogen, a mixture of chalcogens, a mixture of compounds containing a chalcogen and a mixture of a

chalcogen and a compound containing a chalcogen. The chalcogen material is preferably a chalcogen compound such as H_2S, H_2Se, and/or H_2Te, Na_2S, Na_2Se, and/or Na_2Te, and CS_2.

The size of the IF particles produced by the method of the invention is in the nanometer range, typically some tens of nanometers and also hundreds of nanometers. Nanotubes may be even longer.

The IF structures produced by the method of the invention include, but are not limited to, single layer inorganic fullerenes, nested layers inorganic fullerenes, stuffed inorganic fullerenes, single layer nanotubes, nested nanotubes, stuffed nanotubes, inorganic supperlattice structures, and structures with negative curvature (Schwartzites).

In a preferred embodiment, the metal is a transition metal selected from Mo,W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru, more preferably it is Mo.

In a preferred embodiment, the invention relates to a method for the sonoelectrochemical synthesis of inorganic fullerene-like (hereinafter IF) structures of molybdenum sulphide, comprising the steps of:

(a) dissolving in a suitable solvent at least one molybdenum compound and at least one sulphur compound or a sulphur-containing molybdenum compound;

(b) immersing an electrically conductive ultrasonic probe in the solution obtained in (a);

(c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of said electric power supply is connected to a counter electrode;

(d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode: and

(e) recovering the molybdenum sulphide IF structures that precipitated in step (d).

In a most preferred embodiment, the method for sonoelectrochemical liquid phase synthesis of IF-like structures of molybdenum sulphide is carried out at room temperature, comprising the steps of:

(a) dissolving ammonium tetrathiomolybdate in water;

(b) immersing an electrically conductive ultrasonic Ti probe in the solution obtained in (a);

(c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of said electric power supply is connected to a counter electrode;

(d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode, and repeating sequentially the pulses of electric voltage and ultrasonic signal until the desired amount of molybdenum sulphide IF structures is deposited; and

(e) recovering the thus precipitated molybdenum sulphide IF structures.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1. Transmission electron microscopy (TEM) image of the sonoelectrochemically-prepared MoS_2 powder. The inset in the top lefthand corner shows part of the image at x 2 magnification.

Fig. 2. TEM images of the same MoS_2 particle taken with the sample rotated in the direction of the electron beam at an angle of **A** +45°; **B** 0°; **C** -45°.

Fig. 3. TEM image of part of a MoS_2 nanotube.

Fig. 4. TEM image of a large MoS_2 polyhedral structure filled with MoO_2. The inset at the top lefthand corner shows part of the image at x 3 magnification.

DETAILED DESCRIPTION OF THE INVENTION

The invention will be illustrated by the following non-limiting examples and their figures.

Experimental: We used a sonoelectrochemical device similar to the one described by Reisse and co-workers.[15] A titanium horn (liquid processor, 20 kHz)

acts as both the cathode and the ultrasound emitter. The electroactive part of the sonoelectrode is the planar circular surface at the bottom of the horn. A constant current deposition pulse (160 $mAcm^{-2}$) was immediately followed by a sonic pulse (16 W intensity). The on and off times of both current and sonic pulses were the same (0.34 s). A spiral made of platinum wire (0.5 mm diameter and 15 cm long) was used as counter electrode. and the intensity - 16 W. The electrolyte (100 ml) was an aqueous solution of 50 mM ammonium tetrathiomolybdate [$(NH_4)_2MoS_4$] and 1 M sodium sulfate [$NaSO_4$] at a pH of 6.0. The deposition was continued for ca. 90 minutes. At the end of the reaction, the precipitate was centrifuged, washed repeatedly with acetone and dried under vacuum.

A transmission electron microscopy (TEM) image of a sample of this powder is shown in Fig. 1. Although there is considerable variation in the size and shape of the individual particles, they are typically several tens of nm in size and most of the particles have sizes which are the same order of magnitude in all three dimensions. However, there is some variability in the shapes, as can be seen in Fig. 1, where the dimension can be twice as much in one direction as in the others. The crystalline layers (typically between 12 and 15) of MoS_2 can be clearly seen surrounding a featureless core. From such a two-dimensional picture, we cannot tell if the particles are in the form of discs (or cylinders) or whether they are surrounded by the MoS_2 layers in all directions like the $W(Mo)S_2$ fullerene-like structures.

Fig. 2 displays TEM images of the same particle at different orientations to the electron beam. The fact that the molecular layers are seen at different angles is a convincing demonstration of the curved and closed nature of the structures. If the sample were flat, as is normally the case for this material, an image of the layers would be seen only when the layers were aligned with the electron beam. In a closed, curved structure, part of the layers will always be aligned with the beam, regardless of the orientation. By the same argument, the different (002) planes will only be visible when they are approximately parallel to the electron beam, i.e., at the outer portions of the 'spheres'. They will become increasingly less visible

toward the center of the structure. Also, if we assume a roughly spherical shape, the particle will be thicker near the center, resulting in less transmission of the electron beam and loss of information. Therefore we cannot state definitively if these structures are made up entirely of MoS_2 sheets, are hollow or contain a core of another material (MoO_2, amorphous MoS_2). The presence of MoS_2 planes inside the closed structures, but oriented in various directions, as seen in Fig. 2 (and particularly clearly in Fig. 2(c)) suggests that the structures are hollow to some extent. Some of these planes could lie on the outer surface of the structures; however the observation that they almost always terminate within the boundaries of the closed structures suggest that this is less likely.

Occasionally seen, are nanotubes, with the long axis much larger than the cross section (Fig. 3 shows part of one of these nanotubes). Also sometimes seen are larger (>100 nm), irregularly-shaped polyhedral structures (Fig. 4). The number of MoS_2 layers in these larger structures is no greater than in the smaller ones and most of the structure is featureless to TEM. However, ED of the structure in Fig. 4 showed the presence of MoO_2 in addition to MoS_2. X-ray diffraction (not shown) confirmed the presence of MoO_2 (monoclinic, powder pattern 32-671). In addition the (002) reflection of the MoS_2 was shifted slightly to lower angles. The shift to smaller angles compared with normal MoS_2 can be explained either by strain-induced lattice expansion characteristic of closed $Mo(W)S_2$ structures [4,18] or to the presence of oxygen as MoO_xS_2.[19]

Recently, the sonochemical synthesis of MoS_2 has been reported by Mdleleni et al..[20] In this work, $Mo(CO)_6$ and elemental sulphur in tetramethylbenzene were subjected to high intensity ultrasonic radiation. The initially formed MoS_2, which was amorphous, was crystallized by heating at 450°C for 10 hr to give a layered, nanostructured product. In order to check if our MoS_2 could also be formed in the absence of an electrochemical process, our electrodeposition solution was subjected to ultrasonic radiation (16 W continuous radiation for 90 mn). A brown-black powder was formed in the solution. This powder was completely diffraction amorphous (no XRD or electron diffraction pattern could be discerned, even at a

very slow XRD scan rate of 0.15°/mn). On heating to 400°C, a mixture of MoS_2 and various phases of MoO_3 were found by XRD. Therefore, the combination of both electrochemical and ultrasonic processes was necessary to form the crystallized and closed MoS_2 structures from the solution used by us. We note that Mdlelini et al. obtained curved nanostructures in their annealed samples (seen from the TEM micrograph in fig. 2 of their paper). It is possible that their structures are also closed - either partially or completely: however, in the absence of angle-dependent micrographs, this cannot be determined from their paper.

We suggest the following mechanism to explain formation of the closed curved structures. Amorphous MoS_2 is formed by electrodeposition onto the sonic probe cathode. The subsequent sonic shock wave then removes this deposit from the probe surface. The deposit could be spheroidal (nucleating electrodeposits are often nanoparticulate) or planar (crystalline MoS_2 would probably form as sheets, but the amorphous material is less likely to do so). At this point, it is conceivable that the effect of this shock wave is itself sufficient to crystallize the deposit. More probable, however, is that the cause of the crystallization, and possibly bending, which normally require high temperatures, is the collapse of the cavitation bubbles.

Electrodeposition or ultrasonic irradiation alone result in X-ray amorphous Mo-S products, but the combination of both gives well-crystallized closed structures of MoS_2. This technique allows room temperature preparation of large amounts of closed MoS_2 nanoclusters. Ultrasonic radiation is as useful for inducing physical reactions (in this case, crystallization and shaping) as it is for chemical reactions. The combination of electrochemical and sonic processes provide many experimental variables which allow control of particle size, shape, and size and shape distribution and will probably be applicable to the formation of closed structures of other layered compounds which can be prepared by electrochemical (and quite likely also chemical) techniques.

<u>References</u>

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CLAIMS:

1. A method for the sonoelectrochemical liquid-phase synthesis of inorganic fullerene-like (hereinafter IF) structures of metal chalcogenides, wherein said metal is selected from In, Ga, Sn and a transition metal selected from Mo, W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru., and the chalcogen is S, Se or Te, the method comprising the steps of:

(a) dissolving in a suitable solvent: (i) at least one compound of said metal and at least one compound of said chalcogen, or (ii) at least one said chalcogen-containing said metal compound;

(b) immersing an electrically conductive ultrasonic probe in the solution obtained in (a);

(c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of said electric power supply is connected to a counter electrode;

(d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode: and

(e) recovering the IF-metal chalcogenide structures that precipitated in step (d).

2. The method according to claim 1 wherein said suitable solvent in step (a) is aqueous or non-aqueous.

3. The method according to claim 1 or 2, wherein the synthesis is carried out at a temperature in which said solvent is in the liquid state.

4. The method according to claim 3, wherein said solvent is water and the synthesis is carried out at room temperature.

5. The method according to any one of claims 1 to 4, wherein said ultrasonic probe is Ti.

6. The method according to any one of claims 1 to 5, which comprises applying in step (d) first an electric voltage to both the ultrasonic probe electrode and the counter electrode which is then followed by an ultrasonic signal to the ultrasonic probe electrode, and repeating the sequences of electric voltage and ultrasonic signal until the desired amount of IF-metal chalcogenide structures is obtained.

7. The method according to claim 6, wherein the ultrasonic probe electrode is connected to the negative terminal of the electric power supply and the counter electrode to the positive terminal.

8. The method according to any one of claims 1 to 7, wherein the metal is a transition metal selected from Mo,W, V, Zr, Hf, Pt, Re, Nb, Ta, Ti, Cr and Ru.

9. The method according to claim 8, wherein said metal is Mo.

10. A method for the sonoelectrochemical liquid phase synthesis of inorganic fullerene-like (hereinafter IF) structures of molybdenum sulphide, comprising the steps of:

(a) dissolving in a suitable solvent: (i) at least one molybdenum compound with at least one sulphur compound, or (ii) a sulphur-containing molybdenum compound;

(b) immersing an electrically conductive ultrasonic probe in the solution obtained in (a);

(c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of said electric power supply is connected to a counter electrode;

(d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode: and

(e) recovering the molybdenum sulphide IF structures that precipitated in step (d).

11. A method according to claim 10 for room temperature sonoelectrochemical synthesis of inorganic fullerene-like (hereinafter IF) structures of molybdenum sulphide, comprising the steps of:

(a) dissolving ammonium tetrathiomolybdate in water;

(b) immersing an electrically conductive ultrasonic Ti probe in the solution obtained in (a);

(c) electrically connecting the ultrasonic probe, which operates as an electrode, to one terminal of an electric power supply, and the other terminal of said electric power supply is connected to a counter electrode;

(d) applying an ultrasonic signal to said ultrasonic probe electrode and an electric voltage to both the ultrasonic probe electrode and the counter electrode, and repeating sequentially the pulses of electric voltage and ultrasonic signal until the desired amount of molybdenum sulphide IF structures is deposited; and

(e) recovering the thus precipitated molybdenum sulphide IF structures.

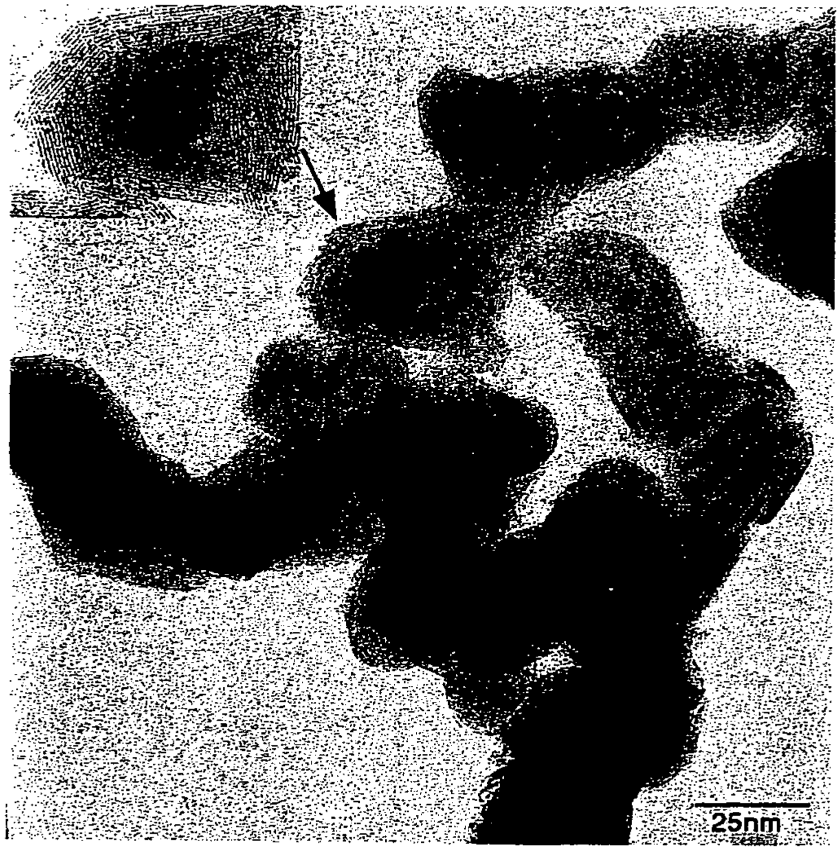

Fig. 1

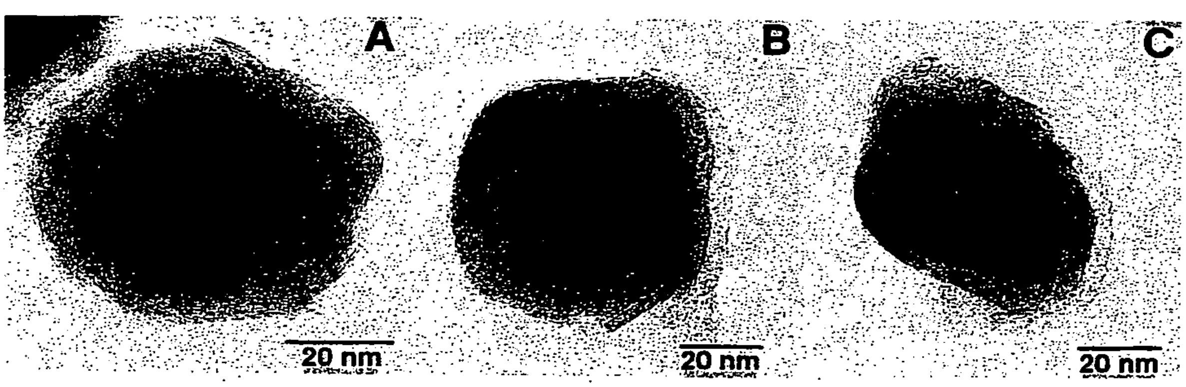

Fig. 2A Fig. 2B Fig. 2C

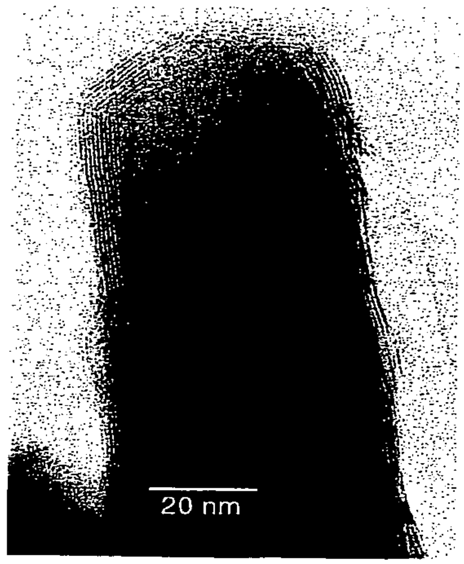

Fig. 3

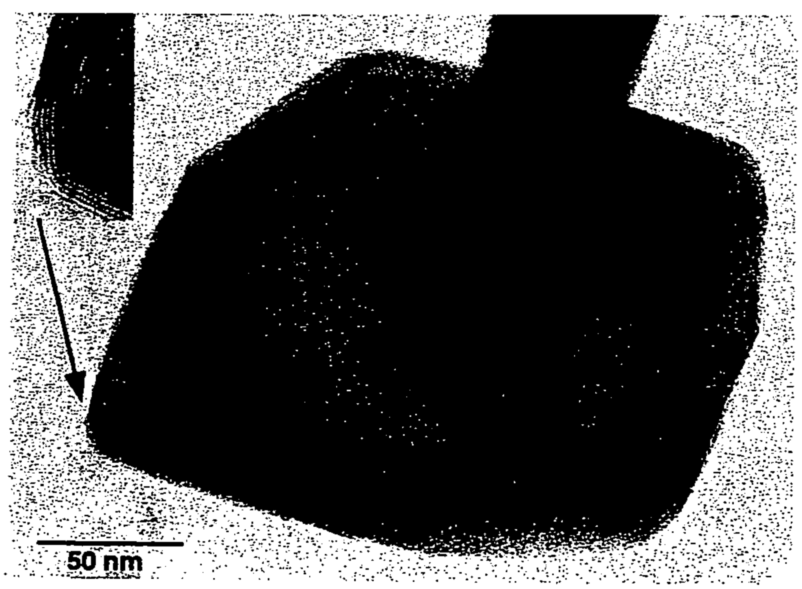

Fig. 4

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PATENT COOPERATION TREATY

REC'D 22 MAR 2001

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PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

14

Applicant's or agent's file reference 9932 PCT	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/IL00/00408	International filing date *(day/month/year)* 12/07/2000	Priority date *(day/month/year)* 13/07/1999
International Patent Classification (IPC) or national classification and IPC C25B1/00		
Applicant YEDA RESEARCH AND DEVELOPMENT CO. LTD. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

   I ☒ Basis of the report
   II ☐ Priority
   III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   IV ☐ Lack of unity of invention
   V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   VI ☐ Certain documents cited
   VII ☐ Certain defects in the international application
   VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
29/01/2001	20.03.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Hahn, H Telephone No. +49 89 2399 8450

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IL00/00408

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:

Description, pages:

1-12 as originally filed

Claims, No.:

1-11 as originally filed

Drawings, sheets:

1/2-2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-11
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-11
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations
   see separate sheet

1. Section V:

The documents of the International Search Report are regarded to be relevant as follows:

D1 = WO 95 33871 A (UNIVERSITE LIBRE DE BRUXELLES) 14 December 1995 (1995-12-14)
D2 = J. REISSE: "Quantitative sonochemistry" ULTRASONICS SONOCHEMISTRY, no. 3, 1996, pages 147-151, XP002153735
D3 = DE 38 26 281 A (HAHN-MEITNER-INSTITUT BERLIN GMBH) 1 February 1990 (1990-02-01)

1.1 Document D1 discloses generally a process and device for the sonoelectrochemical synthesis of compounds (cf. claims 1-14; figure 1) and only mentions the production of copper powder as an example (cf. page 12). Inorganic fullerene-like (IF) structures are neither disclosed nor suggested, let alone those IF structures of the specific metal chalcogenides as defined in claims 1 and 10.

1.2 Document D2 deals generally with sonoelectrochemistry and mentions among many other organic or inorganic products CdTe (cf. page S150, table 2; abstract). Inorganic fullerene-like (IF) structures are neither disclosed nor suggested, let alone those IF structures of the specific metal chalcogenides as defined in claims 1 and 10.

1.3 Document D3 discloses an ultrasonic process for making transition metal chalcogenides of the composition MX_2 (cf. claims 1-8; example). The described process does not include the use of an electrically conductive ultrasonic probe. Furthermore, inorganic fullerene-like (IF) structures are neither disclosed nor suggested, let alone those IF structures of the specific metal chalcogenides as defined in claims 1 and 10.

1.4 The documents D1-D3 thus do neither disclose nor suggest the processes claimed in claims 1 and 10 of the present application. The skilled person cannot get any hint from the aforementioned documents when dealing with the objective technical problem of providing a process for making such IF-structures of the metal chalcogenides in high yields and macroscopic quantities.

1.5 As a consequence of the paragraphs 1.1 to 1.4 above the claims 1-11 meet the requirements of Articles 33(2) and (3) PCT. The industrial applicability is self-evident.

PATENT COOPERATION TREATY

10/030710

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

BEN-AMI, Paulina
YEDA RESEARCH & DEVELOPMENT
CO. LTD
Weizmann Institute of Science
P.O. Box 95
76100 Rehovot
ISRAEL

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing *(day/month/year)* 20.03.2001	
Applicant's or agent's file reference 9932 PCT	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/IL00/00408	12/07/2000	13/07/1999

Applicant
YEDA RESEARCH AND DEVELOPMENT CO. LTD. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

   The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

   Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

   For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Krage, D Tel.+49 89 2399-7580

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תאריך 25 3 2001

Form PCT/IPEA/416 (July 1992)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

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International application No. PCT/IL00/00408	International filing date *(day/month/year)* 12/07/2000	Priority date *(day/month/year)* 13/07/1999

International Patent Classification (IPC) or national classification and IPC
C25B1/00

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   VII ☐ Certain defects in the international application
   VIII ☐ Certain observations on the international application.

Date of submission of the demand 29/01/2001	Date of completion of this report 20.03.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Hahn, H Telephone No. +49 89 2399 8450

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IL00/00408

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:

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- ☐ the description, pages:
- ☐ the claims, Nos.:

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

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6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

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Inventive step (IS)	Yes:	Claims	1-11
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations
see separate sheet

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